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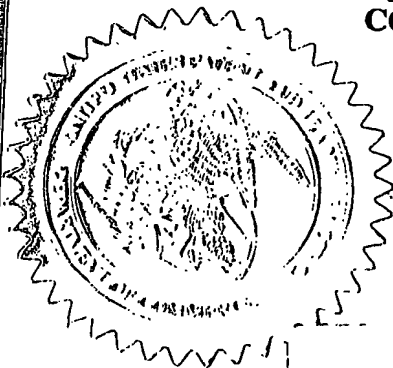
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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60/478936

INVENTOR(S)					
Given Name (first and middle (if any))		Family Name or Surname		Residence (City and either State or Foreign Country)	
Jiang		Zhu		Houston, TX	
<input checked="" type="checkbox"/> Additional inventors are being named on the <u>1</u> separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
FABRICATION OF NANOTUBE REINFORCED EPOXY POLYMER COMPOSITES USING FUNCTIONALIZED SINGLE WALL CARBON NANOTUBES					
Direct all correspondence to:					
CORRESPONDENCE ADDRESS					
<input type="checkbox"/> Customer Number		Type Customer Number here		Place Customer Number Bar Code Label here	
OR					
<input checked="" type="checkbox"/> Firm or Individual Name		Ross Spencer Garsson			
Address		Winstead Sechrest & Minick P.C.			
Address		P.O. Box 50784, 1201 Main Street			
City		Dallas		State Texas	
Country		U.S.A.		ZIP 75250-0784	
		Telephone (512) 370-2870		Fax (512) 370-2850	
ENCLOSED APPLICATION PARTS (check all that apply)					
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<input type="checkbox"/> Drawing(s) Number of Sheets				<input type="checkbox"/> Other (specify)	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE AMOUNT (\$)	
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees				\$80.00	
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:		23-2426			
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.					
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input type="checkbox"/> No.		Office of Naval Research			
<input checked="" type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are:		(Grant No. N00014-03-1-0296)			
		Welch Foundation (Grant No. C-1494)			

Respectfully submitted,

SIGNATURE

Date 06/16/2003

TYPED or PRINTED NAME Ross Spencer Garsson

REGISTRATION NO.
(if appropriate)
Docket Number:

38,150

TELEPHONE (512) 370-2870

11321-P066V1

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

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Docket Number **11321-P066V1**

INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle (if any))	Family or Surname	Residence (City and either State or Foreign Country)
Valery N.	Khabashesku	Houston, TX
Haiqing	Peng	Houston, TX
Enrique V.	Barrera	Houston, TX
John L.	Margrave	Houston, TX

Number 1 of 1

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**Invention Disclosure
to
William Marsh Rice University**

1. **Title should be sufficiently descriptive to aid in identifying the invention:**

Fabrication of Nanotube Reinforced Epoxy Polymer Composites using Functionalized SWNTs

2. **Description of the invention:**

A novel material has been fabricated through implementation of the chemical modification processing of single walled carbon nanotubes

In this work novel epoxy polymer composite materials reinforced by functionalized single-walled carbon nanotubes (f-SWNTs) covalently integrated into the polymer matrix structure have been developed. The f-SWNTs were produced using two chemical methods: (i) acid treatment of SWNTs followed by side wall fluorination, (ii) reactions of terminal diamines with the alkylcarboxyl groups attached to the SWNTs side walls in the course of dicarboxylic acid peroxides treatment. Nanotube reinforced epoxy polymer composites have been prepared by processing via f-SWNTs dispersion, homogeneous mixing and compression molding. Significant mechanical properties enhancement have been achieved through the integration of f-SWNTs. The addition of relatively small quantities (1-2 wt%) of functionalized nanotubes into the epoxy materials resulted in mechanical properties that are unprecedented in conventional epoxy polymer composites technology. (see attached materials)

The fabricated new strong material can be used to improve the existing epoxy composites properties, make materials stronger and tougher. Epoxy composites are widely used in aerospace, automobile, electronics, sports products and ship building industry

Significant improvement of mechanical strength, such as tensile, flexural, modulus, toughness, thermal stability over existing epoxy. Using the functionalized nanotubes as reinforcement for epoxy composites is entirely new.

This new material is developed involving several steps: 1) chemical modification of nanotubes for functionalization; 2) Dispersion and mixing into the epoxy; 3) Fabrication of the composites using molding method.

It is expected that more mechanical property improvement can be achieved through further process optimization for functionalization, dispersion and mixing steps..

We are also extending this process to other polymer systems. Functionalization steps may involve more options based on organic chemistry experience.

3. **Grant or Contract Number:** *If the invention was made in connection with any sponsored research, provide the names of all sponsors, including government, corporate and foundation sponsors. This is important because sponsored research contracts frequently obligate Rice with respect to intellectual property which results from the sponsored research. Provide the full applicable grant or contract number(s). If not sponsored, please indicate by "None."*

Office of Naval Research grant no. N00014-03-1-0296, Carbon Nanotechnology Inc., and the Welch Foundation grant no. C-1494

Improving the Dispersion and Integration of Single-Walled Carbon Nanotubes in Epoxy Composites through Functionalization

Jiang Zhu,[†] J. D. Kim,[‡] Haiqing Peng,[§] John L. Margrave,[§]
Valery N. Khabashesku,^{*,§} and Enrique V. Barrera^{*,†}

Department of Mechanical Engineering and Materials Science, Department of Chemistry and Center for Nanoscale Science and Technology, and Department of Chemical Engineering, Rice University, 6100 Main Street, Houston, Texas 77005-1892

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ABSTRACT

Considerable improvement in the dispersion of purified single-walled carbon nanotubes (SWNTs) in an epoxy composite was obtained through functionalization of the SWNTs by using an optimized $\text{H}_2\text{SO}_4/\text{70\% HNO}_3$ acid treatment and subsequent fluorination. Epoxy composites containing 1 wt % nanotubes were processed by dissolving the functionalized SWNTs in dimethylformamide and mixing with the epoxy resin thereafter. The functionalized nanotubes were observed to be highly dispersed and well integrated in the epoxy composites. The enhancement of mechanical properties of the latter was indicated by a 30% increase in modulus and 18% increase in tensile strength. This work demonstrates the practical use of combining acid treatment and fluorination to achieve functionalization and unroping of SWNTs. The functionalized SWNTs can be integrated into epoxy composites through the formation of strong covalent bonds in the course of epoxy ring-opening esterification and curing chemical reactions.

Introduction. The discovery of nanotubes with unique mechanical, electrical, and thermal properties has led to their use in the development of the next generation of composite materials. The nanotubes are expected to serve as mechanical reinforcements for lightweight composite systems with the further promise of multifunctionality. For instance, SWNTs possess a tensile strength of 50–100 GPa and a modulus of 1–2 TPa; these values are 5 and 10 times greater than those for steel, respectively, at just $1/6$ the weight.^{1–4} However, the potential of using nanotubes as polymer composite reinforcements has not been realized mainly because of the difficulties in processing and the limitation on load transfer. Several fundamental processing challenges must be overcome to enable the applicable reinforcement by nanotubes.⁵ Because of the intrinsic van der Waals attraction of the nanotubes to each other, which is associated with their high aspect ratio (up to 1000), nanotubes are held together as bundles and ropes, having very low solubility in most solvents.⁶ The dispersion property becomes more important

when nanotubes are blended into the polymer. Nanotubes tend to remain as entangled agglomerates, and homogeneous dispersion is not easily obtained. Furthermore, because of the atomically smooth nonreactive surface of nanotubes, the lack of interfacial bonding limits load transfer from the matrix to nanotubes. In this situation, nanotubes are typically pulled out from the matrix rather than fractured and play a limited reinforcement role.⁷ Additional processing difficulties for nanotube-reinforced epoxy composites come from the significant increase in viscosity when the nanotubes are directly added to the epoxy.

A number of recent research efforts have used nanotubes for polymer composites' reinforcement.^{8–16} Some strategies have been proposed to overcome the various barriers for accomplishing dispersion including the use of ultrasonication, high shear mixing, the aid of surfactants, the use of chemical modification through functionalization, wrapping the tubes with polymer chains, and combinations of these. However, to date, very limited success for nanotube-reinforced epoxy composites has been achieved, mainly because of poor dispersion. Dispersion has been more readily accomplished in thermoplastic polymer composites⁸ where stepwise dispersion was aided by high shear mixing, incipient wetting, and elongational flow.

* To whom correspondence should be addressed. E-mail: ebarrera@rice.edu; khval@rice.edu.

[†] Department of Mechanical Engineering and Materials Science.

[‡] Department of Chemical Engineering.

[§] Department of Chemistry and Center for Nanoscale Science and Technology.

Purified multiwalled nanotubes were mixed and dispersed ultrasonically in epoxy resins first by Ajayan et al.⁹ Raman response to tension and compression in cured epoxy composites showed poor load transfer behavior especially under tension. A later study¹⁰ using single-walled nanotubes (SWNTs) at a higher concentration of 5 wt % also showed that the nanotubes were slipping within the bundles and falling apart. Sandler et al.¹¹ reported the difficulty in breaking up the entanglements of the nanotubes although ultrasonication and the intense stirring process improves the dispersion of the nanotubes. Even on the millimeter scale the distribution of nanotubes is not uniform in the epoxy. Vaccarini et al.¹² prepared several epoxy blends and composites with a high concentration (up to 35 wt %) of SWNTs. A linear increase in Young's modulus with the weight percentage of the SWNTs was observed. These authors also pointed out that the possible sliding of the SWNTs within the ropes and the bending of ropes limited further mechanical enhancement because alignment was not produced. Gong et al.¹³ used surfactants as a wetting agent to improve dispersion and observed an improvement in both the mechanical and thermal properties of nanotube epoxy composites. Sean et al.¹⁴ also prepared nanotube epoxy composites by the combination of surfactant and ultrasonication methods for suspending the SWNTs in a large amount of acetone, but no improvement in the modulus and compressive strength for a filament-wound composite with a 1 wt % nanotube addition was found. Microscopy showed a nonuniform dispersion of nanotubes in the epoxy. Biercuk et al.¹⁵ reported a 125% thermal conductivity enhancement and a increase in Vickers hardness by a factor of 3.5 when 2 wt % SWNTs were added to the epoxy.

The use of functionalized nanotubes for epoxy composite fabrication was reported by Tiano et al.¹⁶ The sidewall surfaces of the nanotubes were functionalized via free-radical polymerization of poly(methyl methacrylate). With the 1 wt % load of functionalized nanotubes in the epoxy, an improvement in mechanical properties by an 11% increase in stress and a 21% increase in modulus over those of the unfilled epoxy was demonstrated, which is different from the observed sharp decrease of these parameters when using pristine nanotubes.

Because of poor dispersion and weak interaction between pristine nanotubes and the surrounding matrix, the reinforcing role of high-strength nanotubes in polymer composites is still limited. Chemical modification and functionalization were shown to be feasible and effective means of improving the solubility and dispersion of nanotubes. In addition, functionalized nanotubes can provide bonding sites to the polymer matrix so that the load can be transferred to the nanotubes to prevent separation between the polymer surfaces and nanotubes.¹⁷ Theoretical calculations predicted that even a high degree of sidewall functionalization will degrade the mechanical strength of SWNTs by only 15%.¹⁸

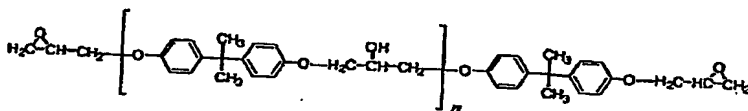
The known chemical routes for the functionalization of nanotubes involve the covalent or noncovalent attachment of various functional groups to either nanotube end-caps or sidewalls.¹⁹⁻⁴³ The end-caps of the SWNTs can be opened

under oxidizing conditions and terminated with the oxygenated functionalities including carboxylic, carbonyl, and hydroxyl groups. Oxidized nanotubes have better solubility and can form well-dispersed electrostatically stabilized colloids in water and ethanol.¹⁹ The presence of carboxylic acid functionalities offers opportunities for further derivatization reactions with a number of molecules. For example, oxidizing acid-treated SWNTs can be further derivatized by reactions with thionyl chloride and long-chain amines²⁰⁻²² or by esterification.^{23,24} In these functionalized materials, the SWNT ropes were reported to be largely exfoliated into individual nanotubes with significantly improved solubility in organic solvents. Furthermore, carboxylic acid groups can undergo esterification reactions with the epoxy. Some cross linking may also take place because both the surface and ends of the nanotube are expected to carry more than one carboxylic acid group. Carbonyl groups on nanotubes can bind to the polymer matrix through hydrogen bonds. Such specific interactions have proven to be effective in promoting mixing for traditional polymer composite applications, and similar success is expected for nanotube-polymer composites.

The direct fluorination of SWNTs and their subsequent derivatization provide a versatile tool for the preparation and manipulation of nanotubes with variable sidewall functionalities.²⁵ Fluorinated nanotubes (F-SWNTs) are appreciably soluble in DMF, THF, and alcohol solvents with a solubility of about 1 mg/mL in 2-propanol.²⁶ The fluorination of nanotubes also dramatically enhances their chemical reactivity and solubility while maintaining their mechanical properties. This makes fluoronanotubes a favorite precursors for our composite applications. Recent studies⁴⁹ have shown that fluorine in F-SWNTs can be efficiently displaced by *N*-alkylamino functionalities. This offers an opportunity for SWNTs to be integrated into the structure of the epoxy system through the sidewall amino functional groups.

As a part of our comprehensive program to develop fully integrated nanotube epoxy composites, the present work is focused on the chemical modification of single-walled carbon nanotubes (SWNTs) in an attempt to achieve high dispersion and enhanced interaction in an epoxy matrix and prepare nanotube-reinforced composites with improved mechanical properties. The functionalization of SWNTs was carried out using two main chemical routes: open-end oxidation and sidewall fluorination. Although both the acid treatment and fluorination methods have been reported, their combined use in nanotube-polymer composite applications has been implemented only in the present work.

Experimental. Materials. Purified SWNT BuckyPearls were provided by Carbon Nanotechnology, Inc. SWNTs were produced by a high-pressure HiPco process and fabricated into millimeter-sized BuckyPearl pellets. This commercial material contains ~13 wt % Fe catalyst. The epoxy resin was a DGEBA epoxy (diglycidyl ether of biphenol A)—EPON 862—obtained from Shell Chemicals. This resin was used in combination with the commercial aromatic diamine EPI-CURE W as a curing agent. The typical molecular structure of DGEBA is shown below:



Anhydrous dimethylformamide (DMF) used as a solvent in the present work was purchased from Fisher Scientific. Air-release agent BYK-555 was obtained from Chemie.

Acid Treatment of SWNTs. For the preparation of end-functionalized SWNTs, we used the oxidizing acid treatment procedure (Scheme 1), being modified in the present work from that developed earlier by Liu et al.⁴² In a typical experiment, SWNTs (500 mg) were immersed in 250 mL of concentrated 3:1 H_2SO_4/HNO_3 . Through a series of experiments with different treatment times, it was determined that 1 h of sonication at room temperature (compared with 24 h for laser ablation produced SWNTs) was optimal for oxidizing HiPco SWNTs. Short-time acid treatment is generally preferred for SWNTs to keep the full length with fewer surface defects. In a final step, HCl was added to the acid mixture to facilitate the terminations of opened ends of the SWNTs with carboxylic acid groups rather than carboxylate.²¹ The solution was extensively washed with water and a NaOH solution. The acid-treated nanotubes (denoted as SWNT-COOH) were collected on a 0.25- μm Millipore membrane by filtration and were dried in a vacuum oven at 70 °C.

Fluorination of SWNT-COOH. Acid-treated nanotubes were fluorinated using a procedure similar to the one developed by Mickelson et al.⁴³ The fluorination was carried out in a Monel reactor heated to 150 °C for 12 h using the conditions required for obtaining the approximate C_2F stoichiometry. The gas-flow ratio for fluorine, hydrogen, and helium was 2:1:30, respectively. The fluorinated acid-treated nanotubes (Scheme 1) were denoted as F-SWNT-COOH.

Dispersion and Composite Preparation. The functionalized nanotubes were dispersed in DMF (2 mg/mL) by sonication for 5 min using a high-power CUP-HORN ultrasonic processor and then for 1 h in an ultrasonic bath (40 kHz). Thereafter, the epoxy resin was added, and the solution was stirred for 30 min. DMF was evaporated at 100 °C in a vacuum chamber. The SWNT/epoxy blend was prepared by stirring for 5 min with a high-shear mixing homogenizer to ensure good homogeneity. A 100:26 ratio of EPI-CURE W curing agent was added, and further stirring was performed with a high-shear mixer. The blend was degassed for 5 h in a vacuum oven and then cast into an aluminum mould. The curing cycle was 2 h at 100 °C under a pressure of 0.3 MPa followed by another 2 h at 160 °C. During mixing, an air-

release agent, BYK-A 555, was added to help reduce porosity.

All nanotube/epoxy composites were prepared using a 1 wt % load of both pristine BuckyPearl SWNTs and functionalized SWNTs. Five dog-bone-shaped specimens were cut and polished for tensile testing. Following the same procedure described above, a control sample from pure epoxy resin was also prepared and tested for comparison.

Characterization. ATR-FTIR and Raman spectroscopy as well as SEM/EDAX analysis were used to characterize the functionalized SWNTs. The inspection of the nanotube dispersion in solvents and epoxy resins was carried out using a ZEISS optical microscope (with a resolution of up to 1 μm). The distribution of nanotubes in the epoxy matrix was visually observed and photographed using a digital camera at a low magnification of 50 \times . The size of nanotube aggregates dispersed in the solvent was measured with a MALVERN instrument Zetasizer 3000 system. This instrument uses dynamic light scattering and can measure particle dispersion sizes ranging from 2 nm to 3 μm . The morphology of the nanotube/epoxy composites was investigated using a Philips scanning electron microscope (SEM) at an accelerating voltage of 30 kV. Fracture surfaces of a nanotube epoxy specimen were sputter-coated with gold prior to their observation. Tensile testing was performed using a screw-driven INSTRON testing machine with a 5 kN load cell according to the ASTM standard D638.

Results and Discussion. *Functionalized SWNTs, Solubility, and Dispersion.* The efficiency of functionalization through the acid treatment and subsequent fluorination was confirmed by ATR-FTIR and Raman spectroscopy. The presence of characteristic bands of the C=O, O-H, and C-O bonds due to the formation of COOH groups predominantly on the open end-tips of the nanotubes after acid treatment is evident in the IR spectrum shown in Figure 1b. The broad band of the C-F stretch appears in the 1220–

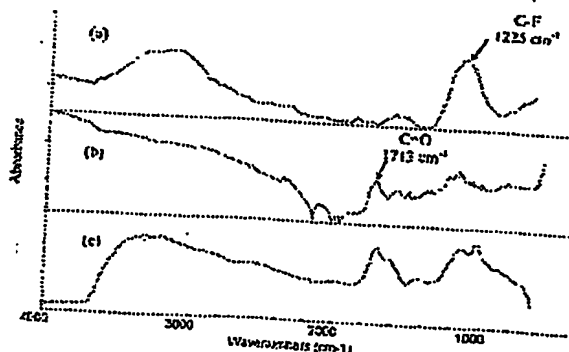
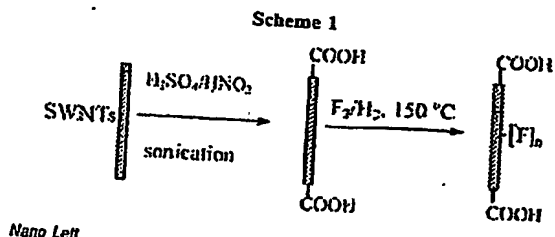


Figure 1. ATR-IR spectra of functionalized nanotubes: (a) F-SWNT, (b) SWNT-COOH, and (c) F-SWNT-COOH.

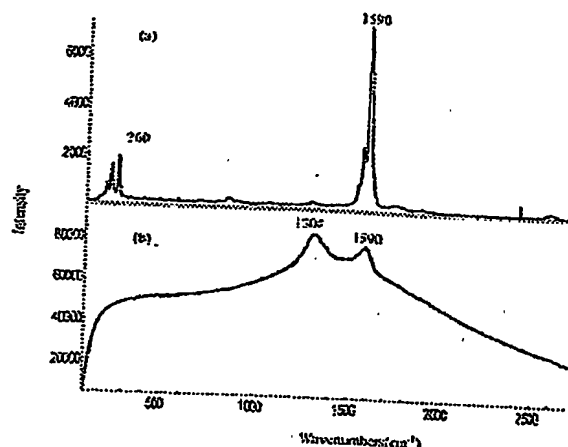


Figure 2. Raman spectra of (a) pristine and (b) functionalized SWNTs.

1250 cm^{-1} region after fluorination of the pristine SWNT (Figure 1a). The carboxylic groups remain intact after the fluorination of the acid-treated SWNTs (SWNT-COOH), as confirmed by the spectrum shown in Figure 1c. The Raman spectrum of pristine SWNTs shows typical breathing modes at 200–260 cm^{-1} and tangential modes at 1590 cm^{-1} (Figure 2a). The appearance of the sp^3 carbon peak at 1301 cm^{-1} after acid treatment and subsequent fluorination (Figure 2b) indicates that the sidewalls of the nanotubes in the F-SWNT-COOH derivative are covalently modified by the attached fluorine. SEM/EDAX elemental analysis of these SWNT derivatives yields an oxygen content of 16 wt % and a fluorine content of 20 wt %, confirming the attachment of fluorine and carboxylic groups to the nanotube framework.

The combination of acid treatment and subsequent fluorination of SWNTs was used in the present work to increase their solubility in the solvent and to facilitate a uniform dispersion in the epoxy resin. It is known that acid oxidation treatment not only results in shortened nanotubes with carboxyl acid groups mainly on the end tips but also leads to smaller-diameter nanotube bundles.^{42,44} Fluorination further improves the solubility due to the interaction of the solvent and fluorine atoms on the surface of nanotubes.^{25,26}

We have shown that functionalized nanotubes can be easily dissolved in DMF within a few minutes under high-power sonication. The optical microscopy pictures, taken to compare the dispersion of functionalized and pristine BuckyPearl nanotubes in DMF, are shown in Figure 3. The 2 mg/mL dispersion of F-SWNT-COOH in DMF is visually non-scattering and homogeneously stable. No precipitation occurred over 4 weeks of standing. The average aggregate size of pristine BuckyPearl nanotubes in DMF (Figure 3a), measured to be 3 μm by the scattering method, was significantly reduced to an average size of 300 nm for functionalized nanotubes (Figure 3b). Because HiPco SWNTs have smaller average diameters (~ 1 nm for the (8, 8) nanotubes) and are more reactive because of higher curvature, they are oxidized more rapidly than the larger-diameter

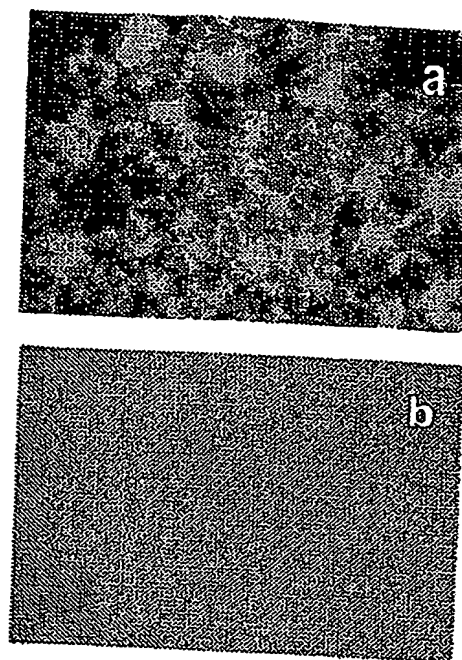
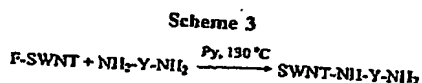
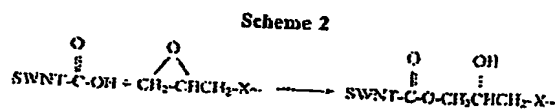


Figure 3. Optical microscopy pictures taken of the nanotube dispersions (2 mg/mL) in DMF: (a) pristine BuckyPearl SWNTs and (b) F-SWNT-COOH.

SWNTs produced by laser ablation.⁴⁵ For this reason, a much shorter acid treatment time should be applied to BuckyPearl nanotubes to preserve their length and prevent the sidewalls from acquiring defects. A series of treatment times ranging from 30 min to 4 h were evaluated, and the solubilities of oxidized SWNTs were compared. It was found that 1 h of sonication treatment is optimal for achieving good solubility of SWNT-COOH in DMF. Functionalized SWNTs also show considerable improvement in dispersion throughout the epoxy matrix in comparison with that of the purified BuckyPearl SWNTs. Only a few large agglomerates were visible by optical microscopy in the dispersions of the former, but many aggregated clusters were observed for the latter. We have also found that special care must be taken to prevent nanotube reaggregation when the solvent is being evaporated and the concentration of nanotubes is high.

Interaction between Nanotubes and the Epoxy Matrix. Carboxyl and fluorine groups covalently attached to the nanotubes offer the opportunity for chemical interactions with the epoxy systems. Therefore, the composite fabrication process can take advantage of the presence of those functional groups. It is known that the epoxy groups can directly react with the carboxylic acid functionalities to form esters.⁴⁶ In the presence of tertiary amines, the epoxy groups are also capable of reacting with the hydroxyl function to form an ether linkage. It was recently demonstrated that fluorine on the sidewalls of fluoronanotubes can be readily displaced by alkylidene amino groups at moderate temperature.⁴⁹ These data suggest that the fluoronanotubes may also



react in situ with the amine curing agents during a high-temperature curing process of the epoxy systems. This means that the incorporation of the fluorinated nanotubes into the epoxy/amine reaction will produce efficient interfacial bonding. The expected esterification reaction of the carboxylic acid functional groups on the nanotubes with the epoxy rings is shown in Scheme 2, where "X" represents the bisphenyl-methylene spacing unit in the epoxy structure. The multiple epoxy functional groups can provide cross-linked coupling of the nanotubes to the epoxy matrix. The expected in situ reaction of fluoronanotubes with a diamine during the high-temperature curing process is shown in Scheme 3, where "Y" represents the hydrocarbon spacing units in the diamines. ATR-IR spectroscopy was used to verify the occurrence of the reactions shown in Schemes 2 and 3. For the reaction with amines, fluoronanotubes were initially dispersed in a variety of commercial diamines such as aliphatic, TETA, EDA, cycloaliphatic, PACM, aromatic, and EPI-CURE W and then heated to 130 °C for 2 h, by analogy with earlier work.⁴⁹ After the reaction, the corresponding diamine was completely removed by extensive washing using ethanol, and the obtained SWNT derivative was subsequently dried overnight. ATR-IR spectra (Figure 4) of the derivatized nanotubes showed the disappearance of C-F bond stretches as a result of the reaction. The new peaks in the 3100–3400 and 2800–3000 cm⁻¹ regions, representing the N–H and C–H stretches, respectively, were observed. These new peaks indicated the displacement of fluorine with the diamino functionality. However, the band intensity of the N–H stretches was quite weak, especially for the long-chain

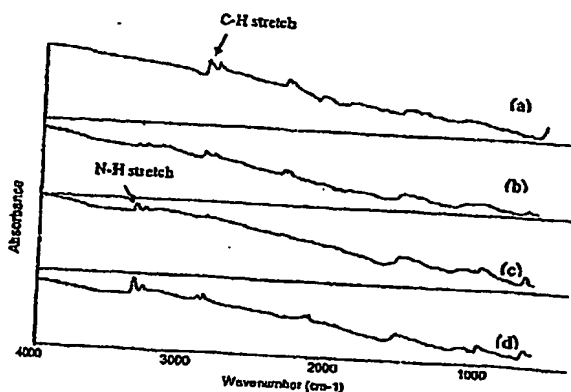


Figure 4. ATR-IR spectra of the SWNT derivatives produced by reactions with several diamines: (a) cycloaliphatic, (b) aromatic, (c) long-chain aliphatic (TETA), and (d) aliphatic (EDA).

Nano Lett.

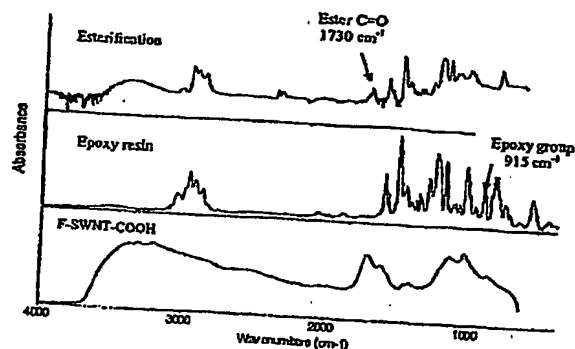


Figure 5. ATR-IR spectra of the functionalized nanotubes (bottom), epoxy resin (middle), and product of the esterification reaction (top).

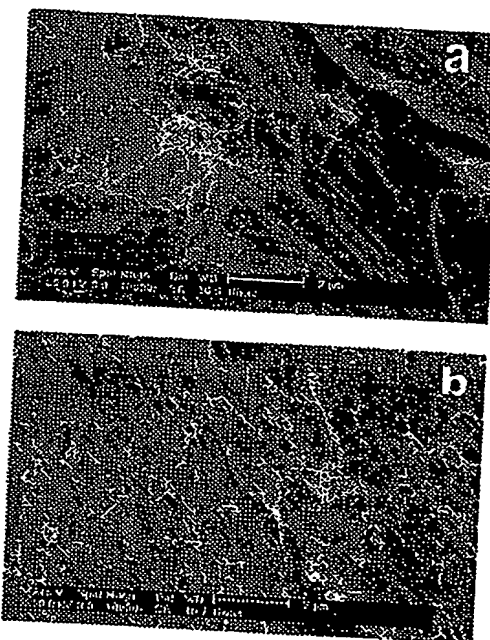


Figure 6. SEM images of fracture surfaces of 1 wt % nanotube/epoxy composites showing dispersed individual nanotube ropes. (a) Nonuniform dispersion of pristine BuckyPearl SWNT in epoxy matrix. (b) Improved dispersion of functionalized nanotube in epoxy matrix.

amines, probably because of cross linking and a tighter bundling of the derivatized nanotubes. For example, in the case of cycloaliphatic diamine (Figure 4a), the C–H stretching bands are observed to be strong, and the N–H modes are very weak. Nevertheless, the SEM/EDAX analysis of the diamino-functionalized nanotubes yielded significant nitrogen content (15–20 wt %). The IR spectrum of the epoxy sample containing the functionalized nanotubes after heating for 2 h at 160 °C shows an intense band at 1730 cm⁻¹, characteristic of the carbonyl (C=O) stretch of the ester derivatives (Figure 5). The epoxy group at 915 cm⁻¹

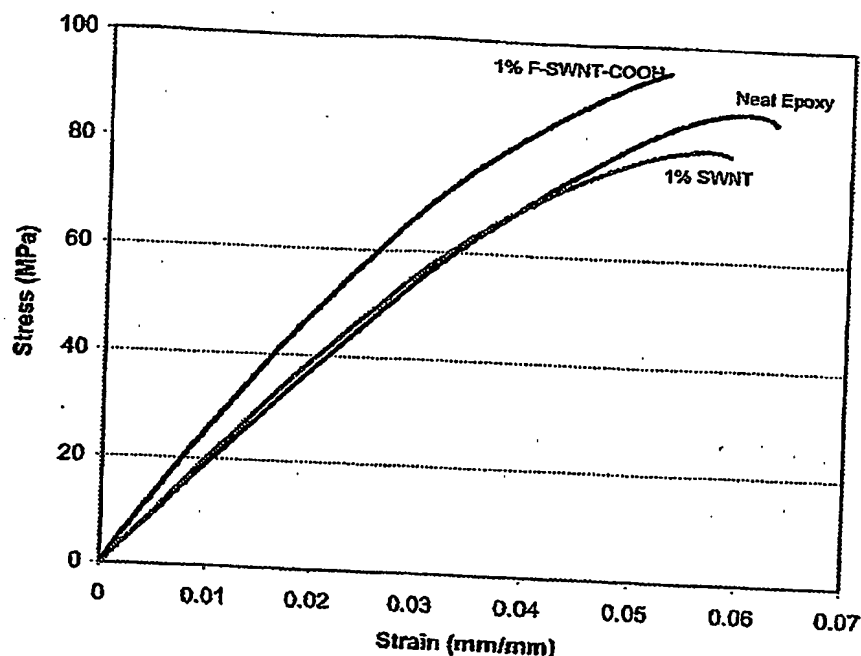


Figure 7. Tensile stress vs strain curves for nanotube/epoxy composites.

Table 1. Average Tensile Strength of Epoxy Composites

epoxy composite formulation	Young's modulus E (MPa)	tensile strength σ (MPa)
neat resin 862/W	2026	83.2
1% BuckyPearl SWNTs	2123	79.9
1% F-SWNT-COOH	2632	95.0

has disappeared, indicating the occurrence of the esterification reaction between the carboxylic acid and epoxy.

These results show that the fluorine and carboxylic acid functional groups grafted onto the nanotubes can provide an in situ chemical integration of the nanotubes into the amine/epoxy system. This type of interaction could improve the interfacial bonding between the nanotubes and the matrix because a similar chemical reaction has been demonstrated in traditional carbon fiber/matrix interface studies.^{47,48}

Microscopic Analysis. The SEM images (Figure 6) of the composite fracture surfaces show the dispersion of the SWNTs in the epoxy matrix. Good homogeneity was achieved for the functionalized nanotubes. A number of bundles were found to break rather than just pull out at the surface, suggesting that bonding exists between the epoxy matrix and SWNTs. By comparison, fracture surfaces of the epoxy composites loaded with the untreated BuckyPearl nanotubes (Figure 6a) show a nonuniform dispersion and the tendency for the nanotubes to entangle as agglomerates. More sliding occurred for the pristine SWNTs in the epoxy matrix, suggesting limited load transfer.

Mechanical Properties. Epoxy composites with a 1 wt % nanotube load have been fabricated using a hot press molding method. Tensile testing was performed to evaluate the effect

of nanotubes on the mechanical properties of an epoxy system. Compared to those of the neat epoxy resin, the mechanical properties showed a very slight change in modulus but a decrease in tensile strength when untreated buckypearl SWNTs (1 wt %) were used directly (Table 1). In comparison, the epoxy composites with 1 wt % functionalized nanotubes had a tensile strength of 95 MPa and a modulus of 2632 MPa, showing 18 and 24% improvements over the epoxy composites with buckypearl SWNTs, respectively. A 30% increase in modulus over that of the neat epoxy resin was measured. The tensile stress versus strain curves are given in Figure 7 for comparison. These results demonstrate that the use of functionalized SWNTs in composites could efficiently enhance reinforcement by improving solubility and dispersion and by chemical bonding to the polymer matrix. Homogeneous dispersion makes more nanotube surfaces available for interaction with the surrounding epoxy matrix. Carboxylic and fluorinated functional groups on the nanotubes provide strong interactions with the epoxy system through esterification and coincident curing; as a result, more effective load transfer to the epoxy matrix could be obtained.

Conclusions. A practical use of chemical modifications of BuckyPearl single-walled nanotubes for the improvement of the dispersion and integration of nanotubes for epoxy composite applications was demonstrated. The combination of acid treatment and fluorination caused both end-tip and sidewall functionalization. With additional help from ultrasonication and high-shear mixing, a high degree of nanotube dispersion in the epoxy matrix can be achieved. The uniformly dispersed and functionalized nanotubes provide for an efficient interaction with the epoxy matrix and thus

Nano Lett.

enhance the overall mechanical properties of the epoxy composites. Mechanical tests confirmed the reinforcing effect of functionalized nanotubes for epoxy composites through the homogeneous dispersion and formation of robust chemical bonds.

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534

Fabrication of Nanotube Reinforced Epoxy Polymer Composites using Functionalized SWNTs

Invention Disclosure by Enrique Barrera, Jiang Zhu, Haiqing Peng, Valery Khabashesku

Department of Mechanical Engineering and Material Science, Department of Chemistry
and Center for Nanoscale Science and Technology,
Rice University, 6100 Main Street, Houston, TX 77005, USA

Abstract

In this work novel epoxy polymer composite materials reinforced by functionalized single-walled carbon nanotubes (f-SWNTs) covalently integrated into the polymer matrix structure have been developed. The f-SWNTs were produced using two chemical methods: (i) acid treatment of SWNTs followed by side wall fluorination, (ii) reactions of terminal diamines with the alkylcarboxyl groups attached to the SWNTs side walls in the course of dicarboxylic acid peroxides treatment. Nanotube reinforced epoxy polymer composites have been prepared by processing via f-SWNTs dispersion, homogeneous mixing and compression molding. Significant mechanical properties enhancement have been achieved through the integration of f-SWNTs. The addition of relatively small quantities (1-2 wt%) of functionalized nanotubes into the epoxy materials resulted in mechanical properties that are unprecedented in conventional epoxy polymer composites technology.

Background

Among polymer composites, epoxy composites are central to the development of future aircraft and spacecraft since the aircraft is becoming more and more of composite and epoxy based system. Nanotube reinforced epoxy systems hold the promise of delivering a superior composite that is lightweight, high strength, tough, impact resistant, and with smart features. A lower content of nanotubes can be added into the composites and they are expected to increase the tensile strength, modulus and the toughness of the epoxy composites by absorbing energy because of their highly flexible elastic behavior [1]. These nanotube reinforced epoxy composites have potential structural applications for space shuttle and space station augmentation and for aircraft components such as a pressure vessel for liquid or gas containment, the leading edges and skins and undersides of wings, control surfaces of airplanes to help protect against damage that might occur from rocks and other debris kicked up during takeoffs and landings. A high electric conductivity hybrid composite system with higher SWNT concentrations could provide lightweight polymer based wiring and interconnects as well as new chip attachment systems for lightweight and more robust electronics.

An important approach to create SWNT composites is to incorporate them via chemical bonding to matrices where they are an integral part of the crosslinked polymer structure [2]. This should enhance load transfer, allow for better dispersion, and it can also enhance

the thermal and electrical properties of the composite thereby creating a multifunctional material. This innovation work presents the first development of the epoxy hybrid composites with direct chemical bonding between the epoxy matrix and the diamine sidewall functionalized SWNTs.



Figure 1. Integration of the nanotubes into the epoxy.

This hybrid is a fully integrated nanotube composite (FINCs) material, where the nanotube is an integral part of the epoxy system and not a separate filler. The first integration idea was realized through the initial acid treatment and fluorination to improve dispersion and integration of the such prepared f-SWNTs via substitution of fluorine on the close-ended nanotubes in the course of reaction with diamines [3]. Another successful approach involved diamine reactions with the alkylcarboxyl groups, directly attached to the SWNTs side walls via a dicarboxylic acid peroxides treatment, to produce terminal amine functional groups capable of curing the epoxy matrix. Other ideas include a direct attachment of epoxy groups to the side chain functionality on the SWNTs, or vinylalkoxysilane treatment of hydroxylated SWNTs, etc. More details are provided on the attached files showing functionalization routes.

Fabrication Process of Nanotube Epoxy Polymer Composites

Materials

The starting material is the purified BuckyPearl SWNTs provided by Carbon Nanotechnology Inc. This material is produced by a HiPco process and has a much more compact form (so called BuckyPearl) with a micrometer scale agglomerates.

The base epoxy resin is a Diglycidyl ether of biphenol A EPON epoxy provided by Shell Chemicals. It was used in combination with an cycloaliphatic and aromatic diamine curing agent.

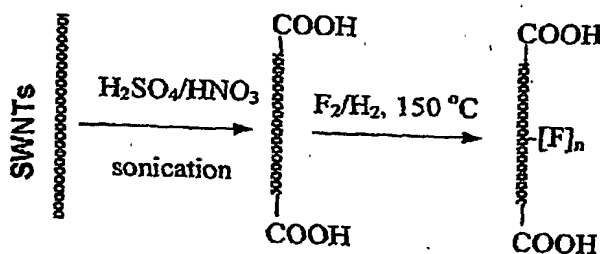
SWNT Functionalization Route # 1: Combined use of acid treatment followed by fluorination

Acid treatment of SWNTs. For preparation of end-functionalized SWNTs we used the oxidizing acid treatment procedure (Scheme 1). It is a modified procedure from the method [4]. 500 mg of SWNTs were sonicated in 250 ml of concentrated H_2SO_4 /70% HNO_3 (3:1) mixture for one hour at room temperature. In a final step, HCl was added into the acid. The solution was extensively washed with water and NaOH solution. The acid treated nanotubes (denoted as SWNT-COOH) were collected on a 0.25 μm Millipore membrane by filtration and dried in the vacuum oven at 70 °C.

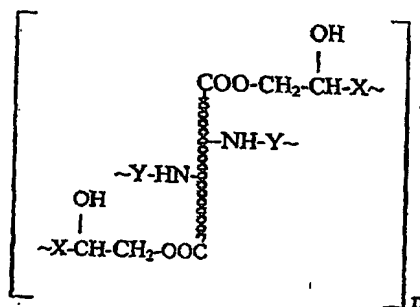
Fluorination of SWNT-COOH. Acid treated nanotubes were fluorinated in a Monel

reactor heated at 150 °C for 12 hours, similar to the fluorination procedure developed earlier for pristine close-ended HiPCO SWNTs [5]. The gas flow ratio for fluorine, hydrogen and helium was 2:1:30. The fluorinated acid treated nanotubes (Scheme 1) were denoted as F-SWNT-COOH.

Scheme 1. Acid treatment following by fluorination



Integration into epoxy system

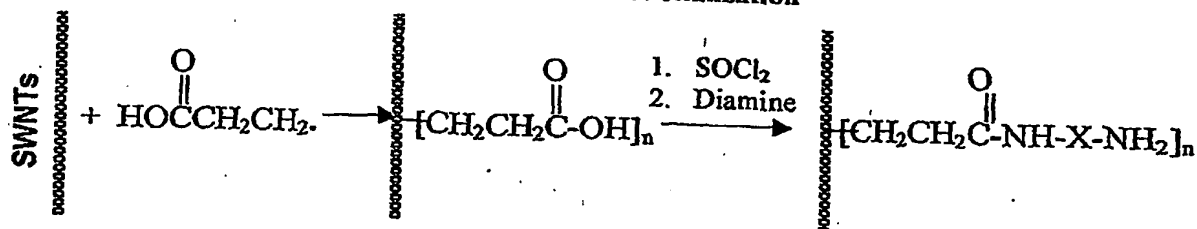


SWNT Functionalization Route #2: Sidewall and end-tip diamine functionalization

Sidewall amine functionalization route is presented on Scheme 2. Buckypearl nanotubes were first treated with HNO_3 yielding a carboxyl groups on SWNTs open ends in order to improve the SWNTs dispersion in epoxy resins. Second step involved the subsequent treatment with dicarboxylic acid peroxides to produce alkylcarboxyl groups attached to the SWNTs side walls according to a procedure described earlier [6,7]. During the third step the acid groups on the SWNTs were subsequently treated with SOCl_2 and diamines. In this work the diamine reaction time was adjusted to one hour to minimize the possible crosslinking of functionalized nanotubes. The amine functionalized nanotubes were denoted as SWNT-X-NH₂.

A variety of diamines include: aliphatic: EDA (Ethylenediamine), TETA (triethylenetetramine), DETA (Diethylenetriamine), D-400 ($\text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{CH}_2-[\text{O}-\text{CH}_2-\text{CH}(\text{CH}_3)]_n-\text{NH}_2$) and cycloaliphatic: PACM and Ancamine 2167 from Air Products; aromatic: EpiCure-W from Shell EPON,

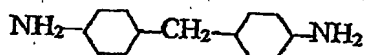
Scheme 2 : Diamine functionalization



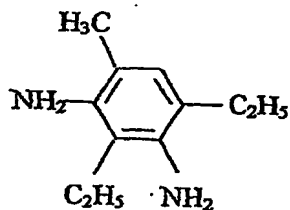
Where "X" represents the internal CH_2 group in different diamine curing agents:

a) Aliphatic diamines (ethelynediamine, TETA, DETA)
 $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

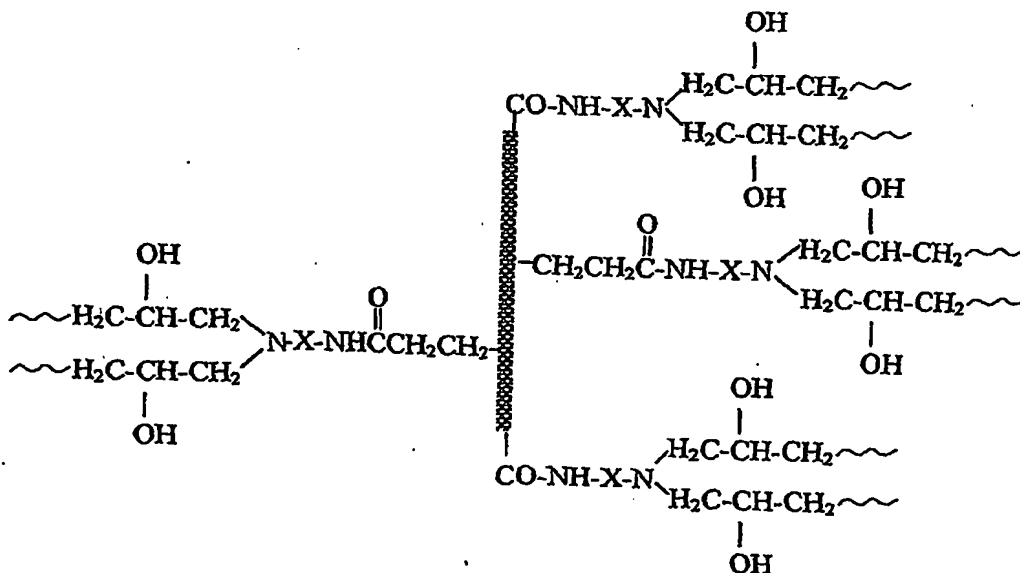
b) Cycloaliphatic diamines: PACM (4,4'-methylenebis(cyclohexylamine))



c) Aromatic diamine (W curing agent)



Integration into the epoxy system



Dispersion and Fabrication of Nanotube Epoxy Composites

The functionalized nanotubes are dispersed in solvent (DMF, ethanol/toluene, chloroform etc.) at a concentration of 2 mg/mL by sonication for 5 mins using a high power CUP-HORN ultrasonic processor and then for one hour in an ultrasonicator bath (40 KHz). Thereafter the epoxy resin is added and the solution is stirred for 10 min. When DMF is used, the mixture is put into a vacuum chamber heated at 100 °C and solvent is evaporated off. When other solvents are used, mixture is put in a hot sonicator (60 °C) bath and sonicated till most solvent is evaporated off. Then the mixture is moved into a vacuum chamber for complete removal of the solvent by vacuum. This procedure produces better dispersion. The SWNTs/epoxy blend without solvent is stirred for 5 min with a high shear mixing homogenizer to ensure good homogeneity. Extensive shear mixing by hand is also applied. A 100/26 ratio of EPI-CURE W curing agent is added then and further stirring performed with a high shear mixer. The blend was degassed for 5 hours in a vacuum oven and then cast into an aluminum mould. Curing cycle is one hour at 100 °C under a pressure of 0.3 MPa in hot press followed for another two hours at 160 °C in oven. During mixing, an air release agent BYK-A 555 is added to help reduce porosity. Nanotube/epoxy composites can be prepared using 1 to 5 wt% load of functionalized SWNTs.

Summary

We have fabricated a fully integrated nanotube epoxy composites (FINC materials) by a novel process. This process includes carbon nanotube sidewall and end-tip functionalization, dispersion and mixing in epoxy, and composite molding processing. Significant improvement in the dispersion of nanotubes in an epoxy was obtained through chemical functionalization. Furthermore, the functionalized nanotubes can be incorporated into epoxy composites through formation of strong covalent bonds in the course of epoxy curing reactions and as a result become an integral component of the crosslinked epoxy system. Functionalized nanotubes therefore play reinforcement role in the epoxy matrix. Epoxy composites with lower content of functionalized nanotubes (1% to 2% wt) have demonstrated the enhanced mechanical properties that are unprecedented in conventional epoxy polymer technology. The tensile strength, modulus, and elongation to failure were improved from 30% to 70% compared with neat EPON 862 epoxy as shown in Figure 2 and Table 1.

The techniques for the integration of SWNT by side-wall and end-tip functionalization for developing a fully integrated epoxy composites can be extended to other polymer systems. A variety of reactive functional groups are capable of attaching covalently to the nanotubes and thus achieving a direct bonding of polymers and SWNTs in nanotube integrated polymer composites.

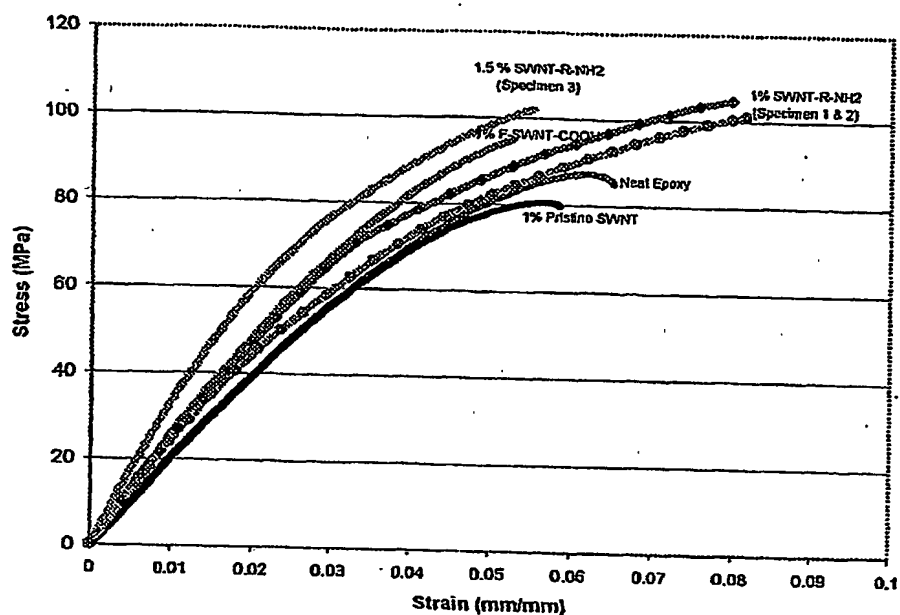


Figure 2. Tensile stress vs. strain curves for nanotube/epoxy composites

Table 1. Tensile properties of nanotube/epoxy composites

Epoxy Composite Formulation	Young's Modulus E (MPa)	Tensile Strength σ (MPa)	Elongation (%)
Neat Resin EPON 862/W	2026	83.2	6.5
1% BuckyPearl SWNTs	2123	79.9	5.8
1% F-SWNT-COOH	2632 (+30%)	95.0 (+20%)	6.3
1% to 2% SWNT-R-NH2	2650 ~ 3400 (+70%)	104 (+30%)	8.2 (+30%)

References:

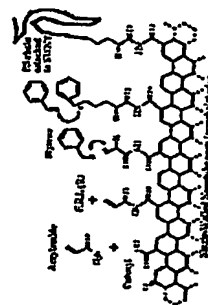
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Achieving Mechanical Properties Enhancement of Nanotube Composites by Integration

Jiang Zhu, Haiqing Peng, Valery N. Khabashesku, and Enrique V. Barrera

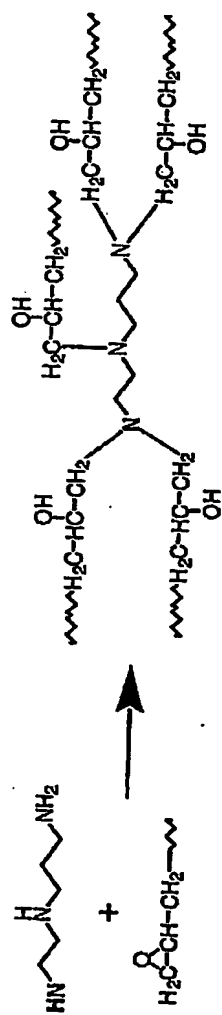
Department of Mechanical Engineering and Materials Science
Rice University

Support by: Carbon Nanotechnologies, Inc.
Office of Naval Research



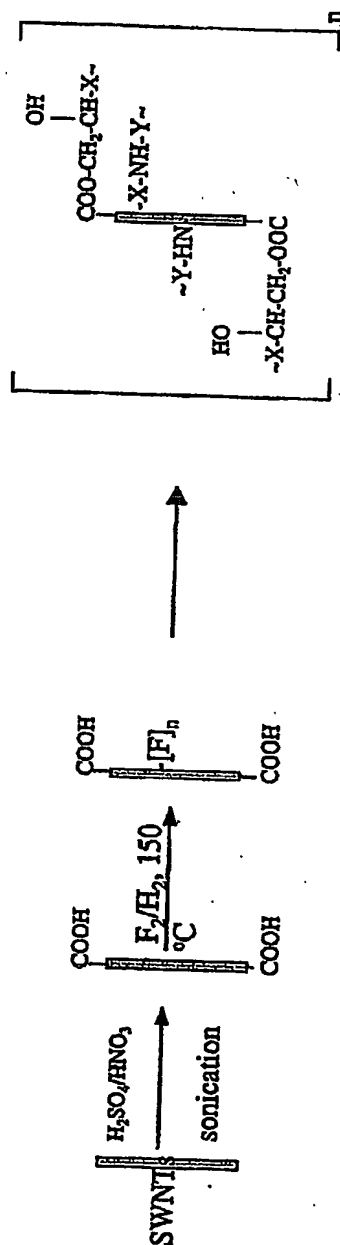
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- Crosslinking reaction between epoxy and amine curing agent



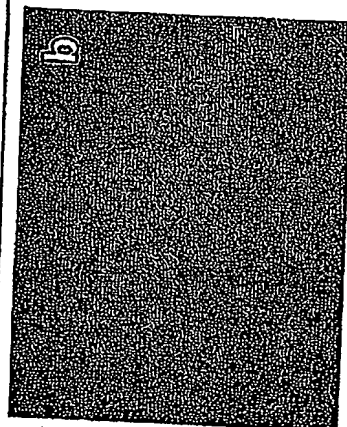
Route #1: Functionalization through Acid Treatment and Fluorination

(Current status: finished and paper published)

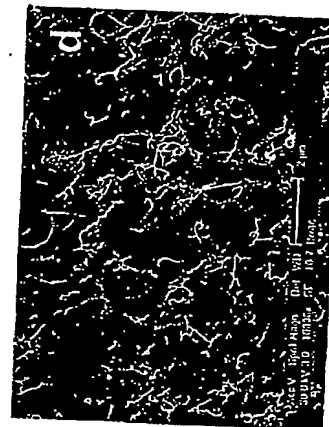
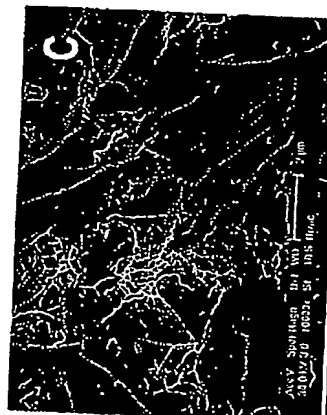


Improving Dispersion and Integration in Epoxy

Dispersion in solvent (DMF)



Fracture surface of 1% SWNT/epoxy composite



(a)(c) Buckypar1 SWNT

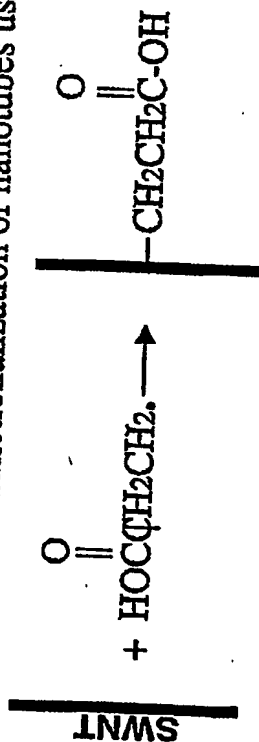
(b)(d) F-SWNT-COOH

Jiang Zhu, et al., Improving the Dispersion and Integration of Single-Walled Carbon Nanotubes in Epoxy Composites Through Functionalization; *NanoLetter*, 2003, (in press)

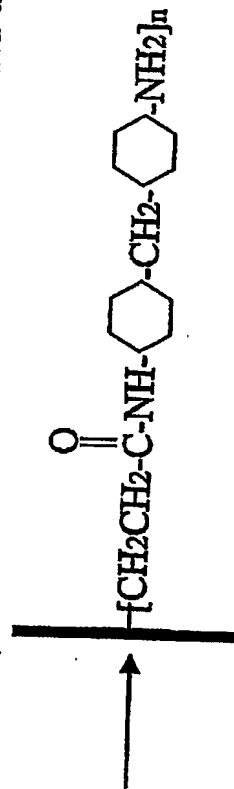
Route #2: Amino-functionalization with Organic Peroxide

(Current status: functionalization achieved and composite prepared)

- (1) Sidewall functionalization of nanotubes using peroxide

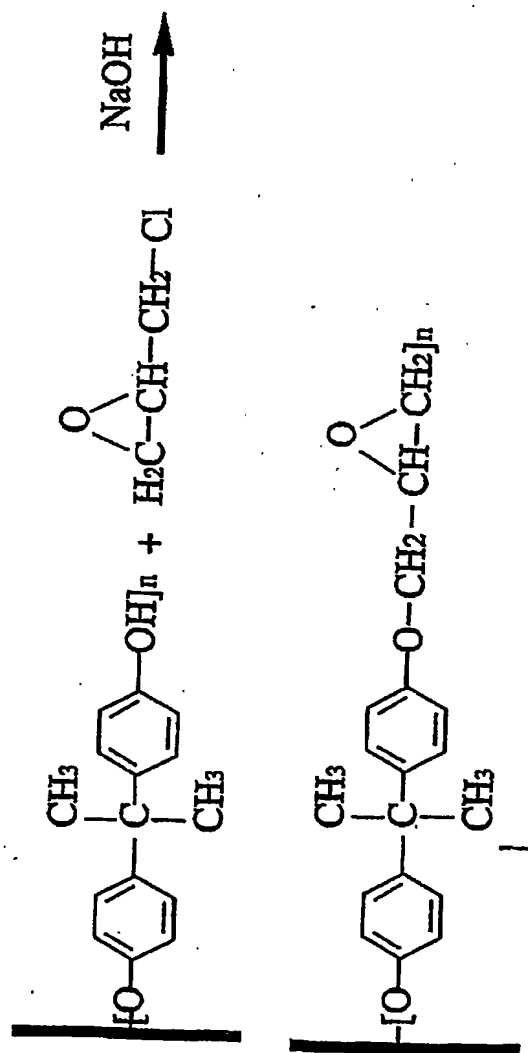


- (2) Attach diamine (PACM) to sidewall of SWNT through SOCl_2 treatment



Route #3: Direct Attachment of Epoxy Group onto Nanotubes

(2) React bisphenol-SWNT with epichlorohydrin to make nanotube-epoxy



Diamine Curing Agent for Epoxies

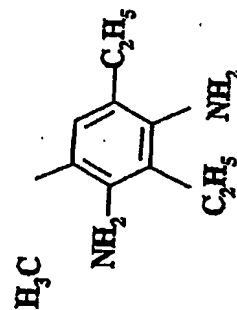
a) Aliphatic diamines (ethylenediamine, TETA, DETA for room temperature cure)



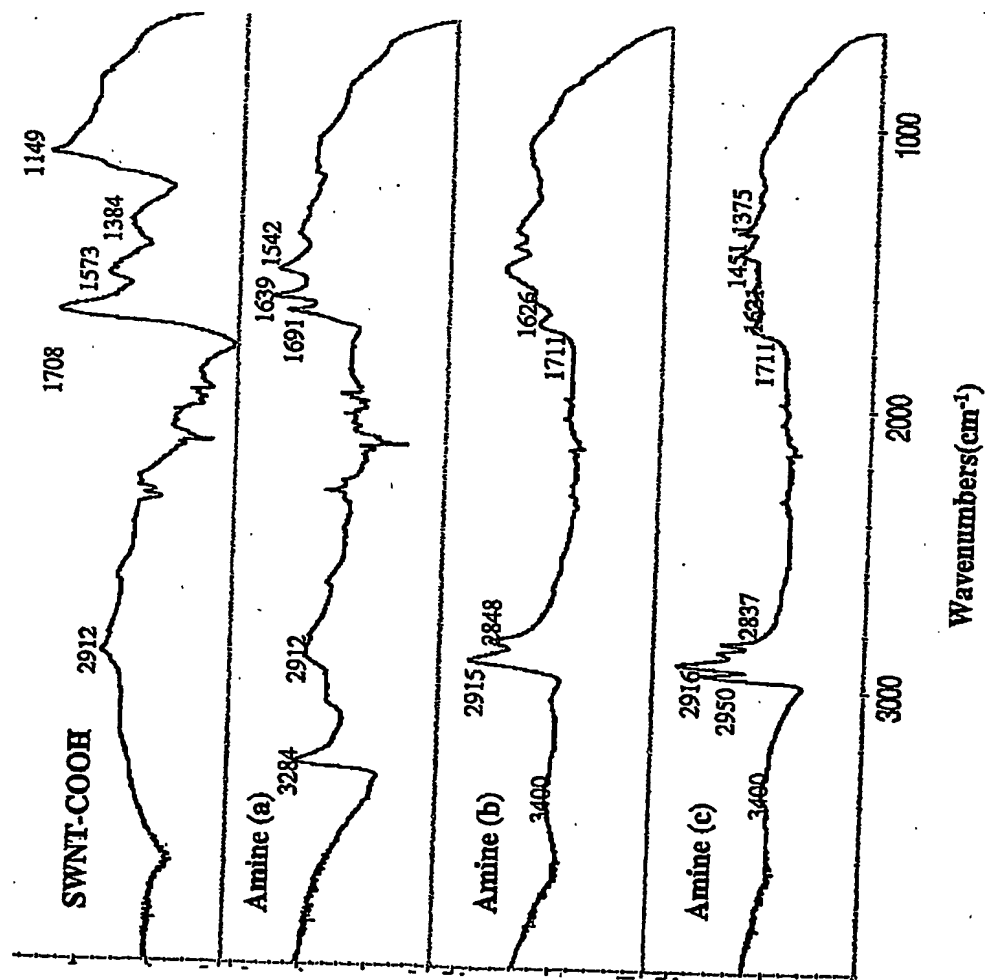
b) Cycloaliphatic diamines: PACM (4,4'-methylenebis(cyclohexylamine))



c) Aromatic diamine (W curing agent, for high temperature cure)

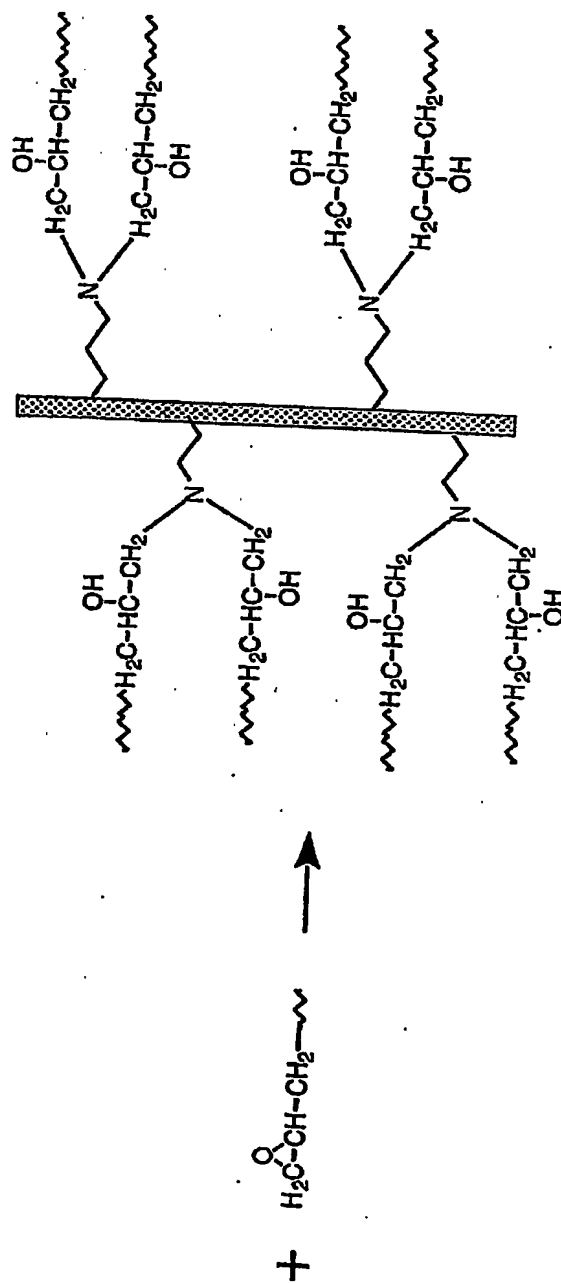


FTIR spectrum of amine-functionalized SWNT

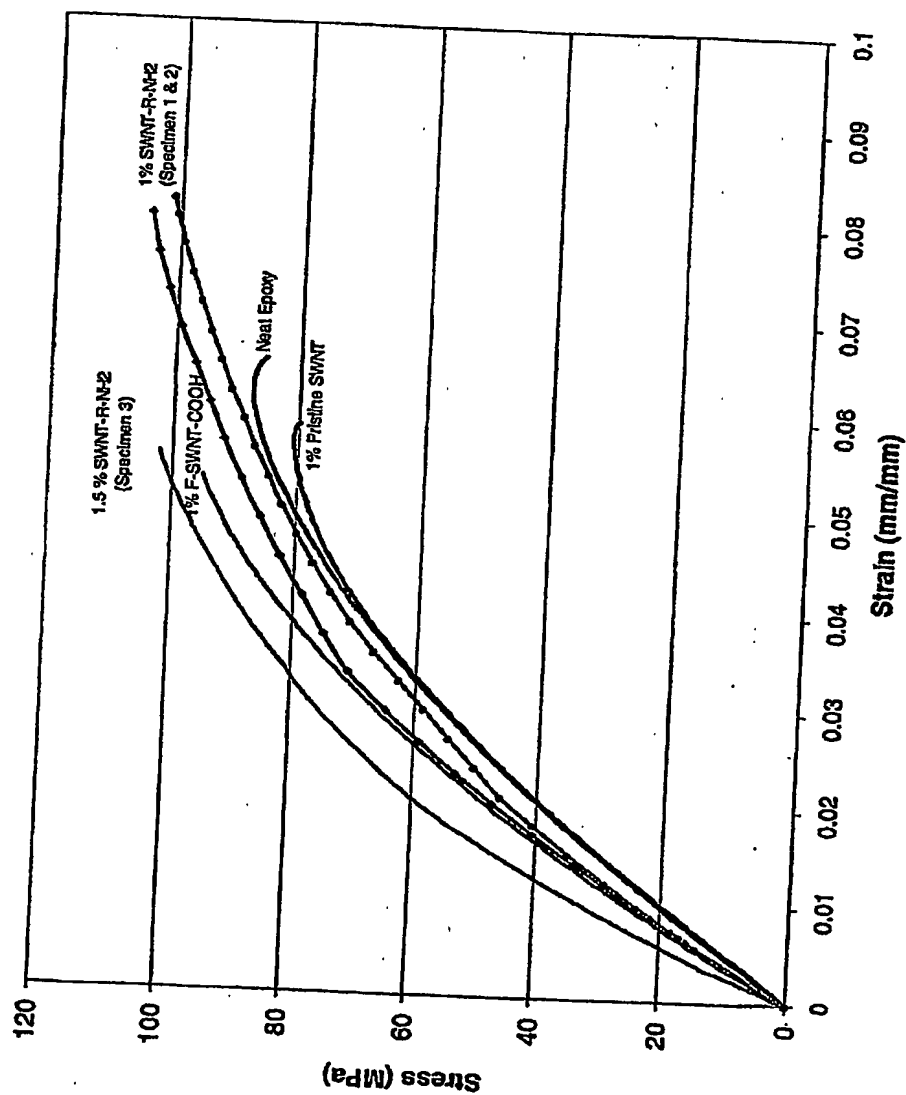


Making Fully-integrated SWNT/epoxy System

(1:20 functionalization achieved, composite prepared and tested)



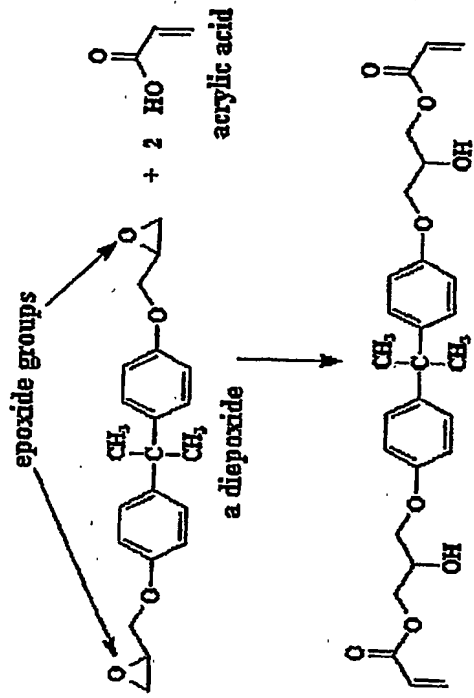
Enhanced Mechanical Properties of Epoxy Composite with Functionalized SWNT



Enhanced Mechanical Properties of Epoxy Composite with Functionalized SWNT

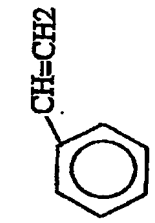
Epoxy Composite Formulation	Young's Modulus E (MPa)	Tensile Strength σ (MPa)	Elongation (%)
Neat epoxy EPON 862/W	2026	83	6.5
1% BuckyPearl SWNTs	2123	80	5.8
1% F-SWNT-COOH	2632 (+30%)	95 (+20%)	6.3
SWNT-R-NH ₂	2650 ~ 3400 (+70%)	104 (+30%)	8.2 (+30%)

Making vinyl ester resin



Epoxy

Vinyl ester



Styrene

Summary

- Tailoring interface by functionalization
- Dispersion and processing for composites
- Comprehensive mechanical properties characterization
- Application to composites

Tailoring interface for nanotube polymer composite

Choosing organosilane coupling agents for thermoset and thermoplastic composites applications:

Polymer	Silanes
Epoxy	amino/epoxy/anhydride functional silanes
Vinyl ester / Polyester	acrylated/methacrylated/vinyl/olefin functional silane
Polystyrene	acrylated/dipodal functional silanes
Polyethylene	amine/vinyl/olefin functional silanes
Polypropylene	acrylate/azide/vinyl/olefin functional silanes

And many more

What is Claimed:

1. A method of integrating single-wall carbon nanotubes into an epoxy matrix comprising the steps of:
 - a) providing a plurality of functionalized single-wall carbon nanotubes;
 - b) dispersing the functionalized single-wall carbon nanotubes in a solvent;
 - c) adding an epoxy resin;
 - d) evaporating the solvent to yield a single-wall carbon nanotube-epoxy blend;
 - e) stirring the single-wall carbon nanotube-epoxy blend with a high-shear mixing homogenizer;
 - f) adding a curing agent; and
 - g) degassing the single-wall carbon nanotube-epoxy blend.
2. The method of Claim 1, wherein the functionalized single-wall carbon nanotubes are carboxylated.
3. The method of Claim 1, wherein the functionalized single-wall carbon nanotubes are alkyl-carboxylated.
4. The method of Claim 1, wherein the functionalized single-wall carbon nanotubes are fluorinated.
5. The method of Claim 1, wherein the functionalized single-wall carbon nanotubes are carboxylated and fluorinated.
6. The method of Claims 2 and 3, wherein the functionalized single-wall carbon nanotubes are reacted with a diamine.
7. The method of Claims 2 and 3, wherein the functionalized single-wall carbon nanotubes react with a curing agent.
8. A method of integrating functionalized single-wall carbon nanotubes into an epoxy matrix comprising the steps of:
 - a) providing a plurality of acid-treated single-wall carbon nanotubes having carboxylic acid groups on their ends;
 - b) fluorinating said acid-treated single-wall carbon nanotubes to yield fluorinated single-wall carbon nanotubes having carboxylic acid groups on their ends;
 - c) dispersing the fluorinated single-wall carbon nanotubes having carboxylic acid groups on their ends in a solvent;
 - d) adding an epoxy resin;
 - e) evaporating the solvent to yield a functionalized single-wall carbon nanotube-epoxy blend;
 - f) stirring the functionalized single-wall carbon nanotube-epoxy blend with a high-shear mixing homogenizer;

- g) adding a curing agent, wherein the the curing agent facilitates integration of the functionalized single-wall carbon nanotubes with the epoxy matrix; and
 - h) degassing the functionalized single-wall carbon nanotube-epoxy blend.
9. A method of integrating functionalized single-wall carbon nanotubes into an epoxy matrix comprising the steps of:
- a) providing a plurality of acid-treated single-wall carbon nanotubes having carboxylic acid groups on their ends;
 - b) treating said acid-treated single-wall carbon nanotubes with dicarboxylic acid peroxides to produce alkylcarboxylated single-wall carbon nanotubes;
 - c) treating the alkylcarboxylated single-wall carbon nanotubes with thionyl chloride to form single-wall carbon nanotubes having acid chloride groups;
 - d) treating the single-wall carbon nanotubes having acid chloride groups with diamine species to yield single-wall carbon nanotubes having amine groups;
 - e) dispersing the single-wall carbon nanotubes having amine groups in a solvent;
 - f) adding an epoxy resin;
 - g) evaporating the solvent to yield a functionalized single-wall carbon nanotube-epoxy blend;
 - h) stirring the functionalized single-wall carbon nanotube-epoxy blend with a high-shear mixing homogenizer;
 - i) adding a curing agent, wherein the the curing agent may facilitate integration of the functionalized single-wall carbon nanotubes with the epoxy matrix; and
 - j) degassing the functionalized single-wall carbon nanotube-epoxy blend.
10. The method of Claim 9, wherein the diamine species is selected from the group consisting of aliphatic diamines, cycloaliphatic diamines, and combinations thereof.

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